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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US98/02720 <b>(22) International Filing Date:</b> 13 February 1998 (13.02.98) <b>(30) Priority Data:</b> 97870028.4 27 February 1997 (27.02.97) EP <b>(34) Countries for which the regional or international application was filed:</b> BE et al. <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventors; and</b> <b>(73) Inventors/Applicants (for US only):</b> ARDIA, Gabriella [IT/IT]; Via E. Vittorini, 103, I-00144 Rome (IT). SCIALLA, Stefano [IT/IT]; Via F.B. Rastrelli, 81, I-00128 Rome (IT). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SOAKER COMPOSITIONS  <b>(57) Abstract</b>  Soaking compositions are disclosed which comprise oxygen bleach, a sorbitan ester in combination with a highly alkoxyated nonionic surfactant. Said compositions are diluted in water to form soaking liquors. The invention is particularly effective in removing particulate soils like silt and clay from fabrics as well as enzymatic stains and/or bleachable stains.		

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## Soaker Compositions

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### Technical Field

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The present invention relates to the cleaning of fabrics in soaking conditions, i.e., in conditions where the fabrics are left to soak in a soaking liquor comprising water and detergent ingredients, typically without undergoing any mechanical agitation, either as a first step before a typical washing operation, or as a single step.

20

### Background of the invention

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Fabric soaking operations have been described in the art. In such soaking operations, fabrics are left in contact with a soaking liquor for a prolonged period of time, typically ranging from a few minutes to overnight or even 24 hours. This laundering process has the advantage that it maximises the contact time between the fabrics and the key active ingredients of the soaking liquor. It also has the advantage that it reduces or eliminates the need for a typical laundering operation involving the need for mechanical agitation, or that it improves the efficiency of the subsequent typical laundering operation.

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Such soaking operations are typically desirable to remove tough outdoor dirt from fabrics, such as particulate soil like mud, silt and/or clays. For example, clays usually have a microcrystalline mineral structure (e.g., hydrous aluminium silicate like illite, montmorillonite, kaolinite and the like) with the presence of an organic fraction. The organic fraction can contain a variety of compounds (e.g., humic acid, fulvic acid, plant/animal biomass and the like). Clays can also contain several kinds of metals (e.g., magnesium, calcium, potassium, iron and

the like). However, such particulate soil is particularly difficult to remove from fabrics. Indeed, it is believed that the very fine dirt grains like clays or silt, typically below 0.002 mm in size, can insert among fabric fibers and steadily stick to the surface of the fibers. This problem is particularly acute with socks  
5 which are most exposed to silt and clay pick-up. Also such soaking operations are not fully satisfactory regarding the stain removal performance delivered on enzymatic stains or even bleachable stains. Enzymatic stains are typically composed of carbohydrates and proteinaceous soil, like blood. It has now been observed that enzymatic stains may act as a glue for particulate soil on  
10 fabrics, thus removing such enzymatic stains may facilitate the removal of particulate soil from fabrics.

It is thus an object of the present invention to improve the stain removal of particulate soils, mud and/or clay, as well as of enzymatic stains and/or  
15 bleachable stains.

It has been found that this object can be met by soaking fabrics in an aqueous soaking liquor comprising an effective amount of a soaking detergent composition comprising an oxygen bleach and a highly  
20 alkoxylated nonionic surfactant, as defined herein after. Indeed, it has been found that such a highly alkoxylated nonionic surfactant and oxygen bleach, in a soaking composition, delivers improved stain removal performance on tough outdoor dirt like particulate soil, enzymatic stains and/or bleachable stains under soaking conditions (i.e., when left in contact for prolonged  
25 period of time typically more than 1 hour up to 24 hours), as compared to the stain removal performance delivered with the same composition being free of such a highly alkoxylated nonionic surfactant. Thus, in its broadest aspect the present invention encompasses a process of soaking fabrics, wherein said fabrics are immersed for more than one hour in a soaking  
30 liquor comprising water and an effective amount of a composition comprising a highly alkoxylated nonionic surfactant and an oxygen bleach, as defined herein, then removed from said soaking liquor.

An advantage of the present invention is that the stain removal  
35 performance, when soaking a fabric in presence of a soaking composition comprising an oxygen bleach and such a highly alkoxylated nonionic

surfactant as defined herein, is improved even in the presence of relatively high levels of hardness ions. Indeed, the presence of hardness ions (calcium or magnesium ions), which occur naturally in the soaking liquor, in particular, can reduce surfactant performance and, eventually precipitate the surfactants from the soaking liquor as a calcium or magnesium salt. This phenomenon occurs less when using an alkoxyated nonionic surfactant as defined herein. Accordingly, the soaking detergent manufacturer may make use of builders which are not the more performing at sequestering free hardness ions, and thus may use less expensive builders in such a soaking composition.

Furthermore, it has been found that the stain removal performance on particulate soil, enzymatic stains and/or bleachable stains is further improved by combining said highly alkoxyated nonionic surfactant and oxygen bleach with a sorbitan ester, as defined hereinafter, in a soaking detergent composition. Thus, the present invention encompasses a soaking detergent composition comprising a sorbitan ester as defined herein, a highly alkoxyated nonionic surfactant as defined herein, and an oxygen bleach, as well as a process of soaking fabrics in a soaking liquor formed with said soaking detergent composition.

An advantage of the present invention is that not only improved particulate soil removal performance is delivered, but also that the soil redeposition on fabrics in prolonged soaking condition is prevented. Furthermore, the soaking compositions of the present invention comprising sorbitan ester, such a highly alkoxyated nonionic surfactant and oxygen bleach also provide effective stain removal performance on other types of stains like greasy stains, e.g., dirty motor oil, spaghetti sauce.

#### Background art

EP-A-736 594 discloses soaking compositions comprising a sorbitan ester in combination with a high amount of a building and soil suspending system comprising a compound selected from citric acid or citrates, silicates, zeolites, polycarboxylates phosphates and mixtures thereof. Oxygen bleach

are include amongst the optional ingredients. No alkoxyated nonionic surfactants are disclosed, nor exemplified.

5                                    Summary of the invention

The present invention encompasses a granular soaking composition comprising:

- 10        - from 0.001% to 15% by weight of the total composition of a sorbitan ester according to the formula  $C_6H_9O_2 (C_2H_4O)_x R_1R_2R_3$ , wherein x is an integer of from 0 to 40,  $R_1$ ,  $R_2$  are independently OH or  $(C_n H_{2n+1})COO$ , and  $R_3$  is  $(C_n H_{2n+1})COO$  group, where n is an integer of from 11 to 17,
- 15        - from 0.001% to 20% by weight of the total composition of an alkoxyated nonionic surfactant according to the formula  $RO-(A)_nH$ , wherein R is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 40 carbon atoms, A is an alkoxy group having from 2 to 10 carbon atoms, and wherein n is an integer from 9 to 100,
- 20        - and an oxygen bleach.

25        The present invention further encompasses a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition as described herein above, for an effective period of time, then removed from said soaking liquor.

30        In its broadest aspect, the present invention encompasses a process of soaking fabrics, wherein said fabrics are immersed for more than one hour in a soaking liquor comprising water and an effective amount of a composition comprising an oxygen bleach and an alkoxyated nonionic surfactant as defined herein, then removed from said soaking liquor.

35                                    Detailed Description of the invention



The present invention encompasses a composition and a process of soaking fabrics. The composition, hereinafter referred to as the soaking composition, is used in the soaking process.

5

A - The composition:

The granular compositions herein comprise at least a sorbitan ester, a particular alkoxylated nonionic surfactant as defined herein and an oxygen bleach.

10

The sorbitan ester:

Accordingly, the first essential ingredient of the compositions of the present invention is a sorbitan ester according to the formula  $C_6H_9O_2 (C_2H_4O)_x R_1R_2R_3$ , wherein x is an integer of from 0 to 40,  $R_1$ ,  $R_2$  are independently OH or  $(C_n H_{2n+1})COO$ , and  $R_3$  is  $(C_n H_{2n+1})COO$  group, where n is an integer of from 11 to 17.

15

In the preferred compositions herein, x is 0 or 20, and the most preferred compositions herein comprise polyethoxylated (20) sorbitan tristearate, i.e.  $C_6H_9O_2 (C_2H_4O)_{20} (C_{17} H_{35}COO)_3$ , or polyethoxylated (20) sorbitan monostearate, i.e.  $C_6H_9O_2 (C_2H_4O)_{20}(OH)_2(C_{17} H_{35}COO)$ , or sorbitan monostearate, i.e.  $C_6H_9O_2(OH)_2(C_{17} H_{35}COO)$ , or sorbitan monopalmitate, i.e.  $C_6H_9O_2(OH)_2(C_{15} H_{31}COO)$ , or mixtures thereof.

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All these materials are commercially available under several trade names, such as Glycosperse TS 20 from Lonza (polyethoxylated sorbitan tristearate), Glycosperse S 20 from Lonza (polyethoxylated sorbitan monostearate), Radasurf 7145 from Fina (sorbitan monostearate), Radasurf 7135 from Fina (sorbitan monopalmitate), Armotan MP from Akzo (sorbitan monopalmitate).

30

It has further been found that combining ethoxylated sorbitan esters with non-ethoxylated sorbitan esters provides better performance than either kind alone.

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The soaking compositions herein comprise from 0.001% to 15% by weight of the total composition of said sorbitan ester or mixtures thereof, preferably from

0.01% to 10%, more preferably from 0.1% to 5% and most preferably from 0.5% to 4%.

5 The nonionic surfactant:

The second essential ingredient of the compositions of the present invention is an alkoxylated nonionic surfactant according to the formula  $RO-(A)_nH$ , wherein R is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 40 carbon atoms, A is an alkoxy group having from 2 to 10 carbon atoms, and wherein n is an integer from 9 to 100, or a mixture thereof.

15 Preferably R is a substituted or unsubstituted, saturated or unsaturated, linear or branched alkyl group or aryl group having from 6 to 40 carbon atoms, preferably from 8 to 25, more preferably from 12 to 20. Typical aryl groups include the C12 -C18 alkyl benzene groups. Preferably n is an integer from 9 to 100, more preferably from 10 to 80 and most preferably from 10 to 30. A preferably is an alkoxy group having from 2 to 8 carbon atoms, preferably from 2 to 5 and more preferably is propoxy and/or ethoxy.

25 Accordingly suitable alkoxylated nonionic surfactants for use herein are Dobanol® 91-10 (R is a mixture of C<sub>9</sub> to C<sub>11</sub> alkyl chains, A is ethoxy, n is 10) Luthensol AT® or AO® surfactants (where R is a mixture of linear C16 to C18 alkyl chain or unbranched C13-C15, A is ethoxy, and n can be 11, 18, 25, 50 or 80), or mixtures thereof. These Dobanol® surfactants are commercially available from SHELL, while the Luthensol® surfactants are available from BASF.

30 Suitable chemical processes for preparing the alkoxylated nonionic surfactants for use herein include condensation of corresponding alcohols with alkylene oxide, in the desired proportions. Such processes are well known to the man skilled in the art and have been extensively described in the art.

Such highly alkoxyated nonionic surfactants are particularly suitable to be used herein as they deliver improved particulate stains removal performance. Indeed, it is speculated that they act as a soil suspending agent, i.e. they allow suspension of particulate soils and prevent/avoid the redeposition of said soils.

The soaking compositions herein comprise from 0.001% to 20% by weight of the total composition of said alkoxyated nonionic surfactant, as defined herein, or a mixture thereof, preferably from 0.01% to 15%, more preferably from 0.1% to 10% and most preferably from 0.5% to 5%.

The oxygen bleach:

As a third essential ingredient, the compositions according to the present invention comprise an oxygen bleach or a mixture thereof. Indeed, oxygen bleaches provide a multitude of benefits such as bleaching of stains, deodorization, as well as disinfectancy. The sorbitan esters and alkoxyated nonionic surfactants as defined herein have a further particular advantage that they are resistant to oxydation by oxygen bleaches. The oxygen bleach in the composition may come from a variety of sources, such as hydrogen peroxide or any of the addition compounds of hydrogen peroxide, or organic peroxyacid, or mixtures thereof. By addition compounds of hydrogen peroxide, it is meant compounds which are formed by the addition of hydrogen peroxide to a second chemical compound, which may be for example an inorganic salt, urea or organic carboxylate, to provide the addition compound. Examples of the addition compounds of hydrogen peroxide include inorganic perhydrate salts, the compounds hydrogen peroxide forms with organic carboxylates, urea, and compounds in which hydrogen peroxide is clathrated.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The alkali metal salt of percarbonate, perborate or mixtures thereof, are the preferred inorganic perhydrate salts for use herein. Preferred alkali metal salt of percarbonate is sodium percarbonate.

Other suitable oxygen bleaches include persulphates, particularly potassium persulphate  $K_2S_2O_8$  and sodium persulphate  $Na_2S_2O_8$ . Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts.

5

Typically, the soaking compositions in the present invention comprise from 0.01% to 80% by weight of the total composition of an oxygen bleach or mixtures thereof, preferably from 5% to 45% and more preferably from 10% to 40%.

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The soaking compositions of the present invention are granular compositions. This compositions can be made by a variety of methods well known in the art, including dry-mixing, spray drying, agglomeration and granulation and combinations thereof. The compositions herein can be prepared with different bulk densities, from conventional granular products to so called "concentrated" products (i.e., with a bulk density above 600g/l).

15

#### Optional ingredients:

20 The soaking compositions of the present invention may further comprise a variety of other ingredients.

Preferably the compositions herein further comprise a bleach activator or a mixture thereof up to 30% by weight of the total composition. Examples of suitable compounds of this type are disclosed in British Patent GB 1 586 769 and GB 2 143 231. Preferred examples of such compounds are tetracetyl ethylene diamine, (TAED), sodium 3, 5, 5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and n-nonanoyloxybenzenesulphonate (NOBS), and acetyl triethyl citrate (ATC) such as described in European patent application 91870207.7. Also particularly preferred are N-acyl caprolactam selected from the group consisting of substituted or unsubstituted benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl

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caprolactam, butanoyl caprolactam pentanoyl caprolactam. The soaking compositions herein may comprise mixtures of said bleach activators.

Preferred mixtures of bleach activators herein comprise n-  
5 nonanoyloxybenzenesulphonate (NOBS) together with a second bleach  
activator having a low tendency to generate diacyl peroxide, but which delivers  
mainly peracid. Said second bleach activators may include tetracetyl ethylene  
diamine (TAED), acetyl triethyl citrate (ATC), acetyl caprolactam, benzoyl  
caprolactam and the like, or mixtures thereof. Indeed, it has been found that  
10 mixtures of bleach activators comprising n-nonanoyloxybenzenesulphonate and  
said second bleach activators, contribute to further boost particulate soil  
removal performance while exhibiting at the same time good performance on  
diacyl peroxide sensitive soil (e.g., beta-carotene) and on peracid sensitive soil  
(e.g., body soils).

15 Accordingly, the soaking compositions herein may comprise from 0% to 15% by  
weight of the total composition of n-nonanoyloxybenzenesulphonate, preferably  
from 1% to 10% and more preferably from 3% to 7% and from 0% to 15% by  
weight of the total composition of said second bleach activator preferably from  
20 1% to 10% and more preferably from 3% to 7%.

The compositions herein may comprise an acidifying system amongst the  
preferred optional ingredients. The purpose of said acidifying system is to  
control the alkalinity generated by the source of available oxygen and any  
25 alkaline compounds present in the wash solution. Said system comprises  
anhydrous acidifying agent, or mixtures thereof, which needs to be  
incorporated in the product in an anhydrous form, and to have a good  
stability in oxidizing environment. Suitable anhydrous acidifying agents for  
use herein are carboxylic acids such as citric acid, adipic acid, glutaric acid,  
30 3 chetoglutaric acid, citramalic acid, tartaric acid and maleic acid or their  
salts or mixtures thereof. Other suitable acidifying agents include sodium  
bicarbonate, sodium sesquicarbonate and silicic acid. Highly preferred  
acidifying systems to be used herein comprise citric acid and/or sodium  
citrate. Indeed, citric acid can be used in its acidic form or in the form of its  
35 salts (mono-, di-, tri- salts) and in all its anhydrous and hydrated forms, or  
mixtures thereof. It may additionally act as a builder and a chelant, and it is

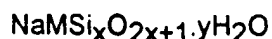
biodegradable. The compositions according to the present invention comprise from up to 20% by weight of the total composition of anhydrous citric acid, preferably from 5% to 15%, most preferably about 10%.

5 The compositions herein may comprise an alkali metal salt of silicate, or mixtures thereof, amongst the preferred optional ingredients. Preferred alkali metal salt of silicate to be used herein is sodium silicate. In the preferred embodiment herein wherein the soaking compositions comprise an oxygen bleach, it has been found that the decomposition of available oxygen produced  
10 in the soaking liquors upon dissolution of the soaking compositions is reduced by the presence of at least 40 parts per million of sodium silicate in said soaking liquors.

Any type of alkali metal salt of silicate can be used herein, including the  
15 crystalline forms as well as the amorphous forms of said alkali metal salt of silicate or mixtures thereof.

Suitable crystalline forms of sodium silicate to be used are the crystalline layered silicates of the granular formula:

20



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20, or mixtures thereof. Crystalline layered sodium silicates of this type  
25 are disclosed in EP-A-164 514 and methods for their preparation are disclosed in DE-A-34 17 649 and DE-A-37 42 043. For the purposes of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the a, b, g and d forms of  $\text{Na}_2\text{Si}_2\text{O}_5$ . These materials  
30 are available from Hoechst AG FRG as respectively NaSKS-5, NaSKS-7, NaSKS-11 and NaSKS-6. The most preferred material is d -  $\text{Na}_2\text{Si}_2\text{O}_5$ , NaSKS-6. Crystalline layered silicates are incorporated in soaking compositions herein, either as dry mixed solids, or as solid components of agglomerates with other components.

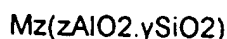
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Suitable amorphous forms of sodium silicate to be used herein have the following general formula:

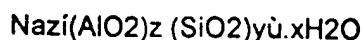


5 wherein M is sodium or hydrogen and x is a number from 1.9 to 4, or mixtures thereof. Preferred to be used herein are the amorphous forms of  $\text{Si}_2\text{O}_5 \text{ Na}_2\text{O}$ .

10 Suitable Zeolites for use herein are aluminosilicates including those having the empirical formula:

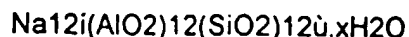


15 wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2; and y is 1; this material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of  $\text{CaCO}_3$  hardness per gram of anhydrous aluminosilicate. Preferred zeolites which have the formula:



20 wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

25 Useful materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the  
30 designations Zeolite A, Zeolite P (B), and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



35

wherein x is from 20 to 30, especially about 27. This material is known as Zeolite A. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

- 5 Typically, the compositions herein may comprise from 0.5% to 15% by weight of the total composition of an alkali metal salt of silicate or mixtures thereof, preferably from 1% to 10% and more preferably from 2% to 7%.

10 The composition herein may also comprise a builder amongst the preferred optional ingredients. All builders known to those skilled in the art may be used herein. Suitable phosphate builders for use herein include sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Other phosphorus builder compounds are disclosed in U.S. Pat. Nos. 3,159,581;  
15 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference.

Suitable polycarboxylate builders for use herein include ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued  
20 April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,120,874 and 4,102,903.

25 Other useful detergency builders include the ether hydroxypolycarboxylates, 1,3,5-trihydroxy benzene-2,4,6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic  
30 acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

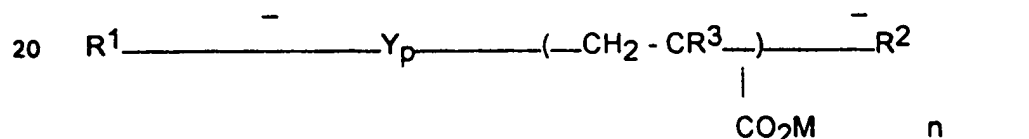
35 Also suitable in the soaking compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in



U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylate builders are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Other suitable polycarboxylate builders for use herein include builders according to formula I



wherein Y is a comonomer or comonomer mixture; R<sup>1</sup> and R<sup>2</sup> are bleach- and alkali-stable polymer-end groups; R<sup>3</sup> is H, OH or C<sub>1-4</sub> alkyl; M is H, alkali metal, alkaline earth metal, ammonium or substituted ammonium; p is from 0 to 2; and n is at least 10, or mixtures thereof.

Preferred polymers for use herein fall into two categories. The first category belongs to the class of copolymeric polymers which are formed from an unsaturated polycarboxylic acid such as maleic acid, citraconic acid, itaconic acid, mesaconic acid and salts thereof as first monomer, and an unsaturated monocarboxylic acid such as acrylic acid or an alpha -C<sub>1-4</sub> alkyl acrylic acid as second monomer. Referring to formula I hereinabove, the polymers belonging to said first class are those where p is not 0 and Y is selected from the acids

listed hereinabove. Preferred polymers of this class are those according to formula I hereinabove, where Y is maleic acid. Also, in a preferred embodiment,  $R^3$  and M are H, and n is such that the polymers have a molecular weight of from 1000 to 400 000 atomic mass units.

5

The second category of preferred polymers for use herein belongs to the class of polymers in which, referring to formula I hereinabove, p is 0 and  $R^3$  is H or  $C_{1-4}$  alkyl. In a preferred embodiment n is such that the polymers have a molecular weight of from 1000 to 400 000 atomic mass units. In a highly preferred embodiment,  $R^3$  and M are H.

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The alkali-stable polymer end groups  $R^1$  and  $R^2$  in formula I hereinabove suitably include alkyl groups, oxyalkyl groups and alkyl carboxylic acid groups and salts and esters thereof.

15

In the above, n, the degree of polymerization of the polymer can be determined from the weight average polymer molecular weight by dividing the latter by the average monomer molecular weight. Thus, for a maleic-acrylic copolymer having a weight average molecular weight of 15,500 and comprising 30 mole % of maleic acid derived units, n is 182 (i.e.  $15,500 / (116 \times 0.3 + 72 \times 0.7)$ ).

20

Temperature-controlled columns at 40°C against sodium polystyrene sulphonate polymer standards, available from Polymer Laboratories Ltd., Shropshire, UK, the polymer standards being 0.15M sodium dihydrogen phosphate and 0.02M tetramethyl ammonium hydroxide at pH 7.0 in 80/20 water/acetonitrile.

25

Of all the above, highly preferred polymers for use herein are those of the first category in which n averages from 100 to 800, preferably from 120 to 400.

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Preferred builders for use herein are polymers of maleic or acrylic acid, or copolymers of maleic and acrylic acid.

35

Typically, the compositions of the present invention comprise up to 50% by weight of the total composition of a builder or mixtures thereof, preferably from 0.1% to 20% and more preferably from 0.5 to 11%.

Preferably the soaking compositions herein further comprise a chelating agent or mixtures thereof. Chelating agents are desired herein as they help to control the level of free heavy metal ions in the soaking liquors, thus avoiding rapid decomposition of the oxygen released by oxygen bleach. Suitable amino carboxylate chelating agents which may be used herein include diethylene triamino pentacetic acid, ethylenediamine tetraacetates (EDTA), N-hydroxyethylethylenediamine triacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraamine hexaacetates, and ethanoldiglycines, alkali metal ammonium and substituted ammonium salts thereof or mixtures thereof. Further suitable chelating agents include ethylenediamine-N,N'-disuccinic acids (EDDS) or alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof. Particularly suitable EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof. Also others suitable chelating agents may be the organic phosphonates, including amino alkylene poly(alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or in the form of their metal alkali salt. Preferably, the organic phosphonate compounds where present are in the form of their magnesium salt.

The soaking compositions in the present invention may accordingly comprise from 0% to 5% by weight of the total compositions of said chelating agents, preferably from 0% to 3%, more preferably from 0.05% to 2%.

The compositions herein may also comprise other surfactants on top of the sorbitan ester and alkoxyated nonionic surfactant as described herein before. Such surfactants may be desirable as they may further contribute to the benefit of the compositions herein: i.e., improved stain removal on particulate soils as well as other types of soils like enzymatic and/or grease.

Such surfactants may be present in the soaking compositions according to the present invention, on top of sorbitan ester and the alkoxyated nonionic surfactant as described herein before, in amounts of from 0.1% to 50% by weight of the total composition, preferably of from 0.1% to 20% and more preferably of from 1% to 10%. Surfactants to be used herein include

nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof.

Suitable anionic surfactant for use herein include water soluble salts or acids of the formula  $\text{ROSO}_3\text{M}$  wherein R preferably is a  $\text{C}_{10}\text{-C}_{24}$  hydrocarbyl, preferably an alkyl or hydroxyalkyl having a  $\text{C}_{10}\text{-C}_{20}$  alkyl component, more preferably a  $\text{C}_{12}\text{-C}_{18}$  alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of  $\text{C}_{12}\text{-C}_{16}$  are preferred for lower wash temperatures (e.g., below about  $50^\circ\text{C}$ ) and  $\text{C}_{16}\text{-C}_{18}$  alkyl chains are preferred for higher wash temperatures (e.g., above about  $50^\circ\text{C}$ ).

Other suitable anionic surfactants for use herein are water soluble salts or acids of the formula  $\text{RO}(\text{A})_m\text{SO}_3\text{M}$  wherein R is an unsubstituted  $\text{C}_{10}\text{-C}_{24}$  alkyl or hydroxyalkyl group having a  $\text{C}_{10}\text{-C}_{24}$  alkyl component, preferably a  $\text{C}_{12}\text{-C}_{20}$  alkyl or hydroxyalkyl, more preferably  $\text{C}_{12}\text{-C}_{18}$  alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are  $\text{C}_{12}\text{-C}_{18}$  alkyl polyethoxylate (1.0) sulfate,  $\text{C}_{12}\text{-C}_{18}\text{E}(1.0)\text{M}$ ,  $\text{C}_{12}\text{-C}_{18}$  alkyl polyethoxylate (2.25) sulfate,  $\text{C}_{12}\text{-C}_{18}\text{E}(2.25)\text{M}$ ,  $\text{C}_{12}\text{-C}_{18}$  alkyl polyethoxylate (3.0) sulfate  $\text{C}_{12}\text{-C}_{18}\text{E}(3.0)$ , and  $\text{C}_{12}\text{-C}_{18}$  alkyl

polyethoxylate (4.0) sulfate  $C_{12}-C_{18}E(4.0)M$ , wherein M is conveniently selected from sodium and potassium.

Other anionic surfactants useful for deterative purposes can also be used herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap,  $C_9-C_{20}$  linear alkylbenzenesulfonates,  $C_8-C_{24}$  olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179,  $C_8-C_{24}$  alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as  $C_{14-16}$  methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated  $C_{12}-C_{18}$  monoesters) diesters of sulfosuccinate (especially saturated and unsaturated  $C_6-C_{14}$  diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula  $RO(CH_2CH_2O)_kCH_2COO-M^+$  wherein R is a  $C_8-C_{22}$  alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Other anionic surfactants suitable to be used herein may also include those according to the formula  $R-SO_3M$ , wherein R is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 40 carbon atoms and M is H or a cation. Preferably

R is a substituted or unsubstituted, saturated or unsaturated, linear or branched alkyl group having from 6 to 40 carbon atoms, preferably from 8 to 30, more preferably from 10 to 25 and most preferably from 12 to 18. Preferably M is a cation which can be for example a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc), ammonium or substituted-ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine and mixtures thereof and the like). Suitable anionic sulphonates to used herein are sodium paraffin sulphonate. They may be commercially available from Hoescht under the name of Hostapur® or Hostatat®.

The compositions herein may further comprise a filler like inorganic filler salts such as alkali metal carbonates, bicarbonates and sulphates. Such fillers for instance sodium bicarbonate, may also act as acidifying agent as described herein after. Accordingly, sodium bicarbonate and sodium sulphate are the preferred filler materials for use herein.

Typically, the compositions of the present invention comprise up to 50% by weight of the total composition of a filler or mixtures thereof, preferably from 0.1% to 20% and more preferably from 0.5 % to 10%.

The compositions herein typically also comprise an enzyme or a mixture thereof. Preferably the compositions herein comprise a protease or mixtures thereof. Protease enzymes are usually present in preferred embodiments of the invention at levels sufficient to provide from 0.005 to 0.2 Anson units (AU) of activity per gram of composition. The proteolytic enzyme can be of animal, vegetable or, preferably microorganism preferred origin. More preferred is serine proteolytic enzyme of bacterial origin. Purified or nonpurified forms of enzyme may be used. Proteolytic enzymes produced by chemically or genetically modified mutants are included by definition, as are close structural enzyme variants. Particularly preferred by way of proteolytic enzyme is bacterial serine proteolytic enzyme obtained from *Bacillus*, *Bacillus subtilis* and/or *Bacillus licheniformis*. Suitable commercial

proteolytic enzymes include Alcalase®, Esperase®, Durazym®, Savinase®, Maxatase®, Maxacal®, and Maxapem® 15 (protein engineered Maxacal); Purafect® and subtilisin BPN and BPN' are also commercially available. Preferred proteolytic enzymes also encompass modified bacterial  
5 serine proteases, such as those described in European Patent Application Serial Number 87303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme, which is called "Protease  
10 A" herein. More preferred is what is called herein "Protease C", which is a triple variant of an alkaline serine protease from *Bacillus* in which tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958.4, corresponding to WO 91/06637, Published May 16, 1991,  
15 which is incorporated herein by reference. Genetically modified variants, particularly of Protease C, are also included herein.

Also suitable for use herein is a protease herein referred to as "Protease D" which is a carbonyl hydrolase variant having an amino acid sequence not  
20 found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76 in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +107 and  
25 +123 in *Bacillus amyloliquefaciens* subtilisin as described in the concurrently filed patent applications of A. Baeck, C.K. Ghosh, P.P. Greycar, R.R. Bott and L.J. Wilson, entitled "Protease-Containing Cleaning Compositions" having U.S. Serial No. 08/136,797 (P&G Case 5040), and "Bleaching Compositions Comprising Protease Enzymes" having U.S. Serial  
30 No. 08/136,626, which are incorporated herein by reference.

Some preferred proteolytic enzymes are selected from the group consisting of Savinase®, Esperase®, Maxacal®, Purafect®, BPN', Protease A and Protease B, and mixtures thereof. Bacterial serine protease enzymes  
35 obtained from *Bacillus subtilis* and/or *Bacillus licheniformis* are preferred.

Particularly preferred are Savinase ®, Alcalase ®, Protease A and Protease B.

Typically the compositions herein also comprise an amylase or a mixtures thereof. Engineering of enzymes for improved stability, e.g. oxidative stability is known. See, for example J. Biological Chem., vol. 260, No. 11, June 1985, pp 6518-6521. "Reference amylase" hereinafter refers to an amylase outside the scope of the amylase component of this invention and against which stability of any amylase within the invention can be measured.

The present invention thus makes use of amylases having improved stability in detergents, especially improved oxidative stability. A convenient absolute stability reference-point against which amylases used in the instant invention represent a measurable improvement is the stability of TERMAMYL (R) in commercial use in 1993 and available from Novo Nordisk A/S. This TERMAMYL (R) amylase is a "reference amylase". Amylases within the spirit and scope of the present invention share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g. to hydrogen peroxide/tetraacetylenediamine in buffered solution at pH 9-10; thermal stability, e.g. at common wash temperatures such as about 60°C; or alkaline stability, e.g. at a pH from about 8 to about 11, all measured versus the above-identified reference-amylase. Preferred amylases herein can demonstrate further improvement versus more challenging reference amylases, the latter reference amylases being illustrated by any of the precursor amylases of which the amylases within the invention are variants. Such precursor amylases may themselves be natural or be the product of genetic engineering. Stability can be measured using any of the art-disclosed technical tests. See references disclosed in WO 94/02597, itself and documents therein referred to being incorporated by reference.

In general, stability-enhanced amylases respecting the invention can be obtained from Novo Nordisk A/S, or from Genencor International.



Preferred amylases herein have the common ability of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* alpha-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors.

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As noted, "oxidative stability-enhanced" amylases are preferred for use herein. Such amylases are non-limitingly illustrated by the following:

- 10 (a) An amylase according to the hereinbefore incorporated WO/94/02597, Novo Nordisk A/S, published February 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine (preferably threonine), of the methionine residue located in position 197 of the *Bacillus licheniformis* alpha-amylase, known as TERMAMYL (R), or the homologous position variation of a similar parent amylase, 15 such as *Bacillus amyloliquefaciens*, *Bacillus subtilis*, or *Bacillus stearothermophilus*;
- 20 (b) Stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17, 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *Bacillus licheniformis* NCIB8061. Methionine (Met) was identified 25 as the most likely residue to be modified. Met was substituted, one at a time, in positions 8,15,197,256,304,366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE (R) and SUNLIGHT (R); Such enzymes are 30 commercially available from Genencor under the trade name Plurafact Oxam ®.
- 35 (c) Particularly preferred herein are amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S. These amylases do not yet have a tradename but are those referred to

by the supplier as QL37+M197T. Such enzymes are commercially available under the trade name SP 703 from Novo.

5 Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases.

10 The soaking compositions herein may also comprise a soil suspending agent or a mixture thereof, typically at a level up to 20% by weight, preferably from 0.1% to 10%, more preferably from 0.5% to 2%. Suitable soil suspending agents include ethoxylated diamines, ethoxylated polyamines, ethoxylated amine polymers as described in EP-A-112 593, incorporated herein by reference. Preferred soil suspending agents to be used herein include ethoxylated polyethyleneamine having a molecular weight of from  
15 140 to 310 prior ethoxylation, ethoxylated 15-18 tetraethylenepentamine, ethoxylated 15-18 polyethylenamine, ethoxylated 15-18 ethylenediamine, ethoxylated polyethyleneimine having a molecular weight of from 600 to 1800 prior ethoxylation, and mixtures thereof.

20 Soaking compositions of the present invention may further comprise other optional ingredients such optical brighteners, other enzymes, other chelants, dispersants, soil release agents, photoactivated bleaches such as Zn phthalocyanine sulphonate, dyes, dye transfer inhibitors, pigments, perfumes and the like. Said optional ingredients can be added in varying amounts as  
25 desired.

B - The process:

30 The present invention encompasses processes of soaking fabrics. Indeed, the present invention encompasses a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition as described herein before, for an effective period of time, then removed from said soaking liquor.

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As used herein, the expression "process of soaking fabrics" refers to the action of leaving fabrics to soak in a soaking liquor comprising water and a composition as described herein above, for a period of time sufficient to clean said fabrics. In contrast to typical laundering operation using a washing machine, the soaking process herein allows prolonged contact time between the fabrics and the soaking liquor, typically up to 24 hours. The soaking process can be performed independently from any other process, such as a typical laundering operation, or a first step before a second, typical laundering step. In the preferred soaking processes of the invention, fabrics are left to soak for a period of time ranging from 10 minutes to 24 hours, preferably from 30 min to 24 hours, more preferably more than 1 hour to 24 hours, even more preferably 2 hours to 24 hours, and most preferably 4 hours to 24 hours. After the fabrics have been immersed in said soaking liquor for a sufficient period of time, they can be removed and rinsed with water. The fabrics can also be washed in a normal laundering operation after they have been soaked, with or without having been rinsed in-between the soaking operation and the subsequent laundering operation.

In the soaking process herein, a soaking composition described hereinabove is diluted in an appropriate amount of water to produce a soaking liquor. Suitable doses may range from 40 to 55 grams of soaking composition in 3.5 to 5 liters of water, down to 90 to 100 grams of soaking composition in 20 to 45 liters of water. Typically one dose is 40-55 grams in 3.5 to 5 liters for a concentrated soak (bucket/sink). For washing machine soaked, the dose is 90-100 grams in about 20 (Europe) to 45 (US) liters of water. The fabrics to be soaked are then immersed in the soaking liquor for an appropriate period of time. There are factors which may influence overall performance of the process on particulate dirt/soils. Such factors include prolonged soaking time. Indeed, the longer fabrics are soaked, the better the end results. Ideally, soaking time is overnight, i.e., 8 hours up to 24 hours, preferably 12 hours to 24 hours. Another factor is the initial warm or warm-luke temperature. Indeed, higher initial temperatures of the soaking liquors ensure large benefits in performance.

The process herein is suitable for cleaning a variety of fabrics, but finds a preferred application in the soaking of socks, which are particularly exposed to silt and clay pick-up.

In its broadest aspect the present invention encompasses a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition comprising an oxygen bleach and an alkoxylated nonionic surfactant according to the formula  $RO-(A)_nH$ , wherein R is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 40 carbon atoms, A is an alkoxy group having from 2 to 10 carbon atoms, and wherein n is an integer from 9 to 100, for more than 1 hour, preferably 2 hours to 24 hours and more preferably 4 hours to 24 hours, then removed from said soaking liquor. Indeed, it has been found that when adding such a highly alkoxylated nonionic surfactant in an oxygen bleach-containing soaking composition, improved particulate soil removal as well as improved enzymatic stain removal is obtained.

The stain removal performance test method:

The stain removal performance of a given composition on a soiled fabric under soaking conditions, may be evaluated by the following test method.

- 5 Soaking liquors are formed by diluting for instance 45 g of the soaking compositions herein in 3.78 liter of water or 90g of the soaking composition in 45 liters of water. Fabrics are then immersed in the resulting soaking liquor for a time ranging from more than 1 hour to 18 hours. Finally, the fabrics are removed from the soaking liquors, rinsed with water and washed with a regular washing process, handwash or washing machine wash, with a regular detergent, with or without re-using the soaking liquor, then said fabrics are left to dry.

- 15 For example, typical soiled fabrics to be used in this stain removal performance test may be commercially available from EMC (Empirical Manufacturing Company) Cincinnati, Ohio, USA, such as clay, grass, spaghetti sauce, gravy, dirty motor oil, make-up, barbecue sauce, tea, blood on two different substrates: cotton (CW120) and polycotton (PCW28).

- 20 The stain removal performance may be evaluated by comparing side by side the soiled fabrics treated with the soaking composition according to the present invention with those treated with the reference, e.g., the same composition without such highly alkoxylated nonionic surfactant according to the present invention. A visual grading scale may be used to assign differences in panel score units (psu), in a range from 0 to 4.

The following examples will further illustrate the present invention.

Examples

The following compositions are prepared by mixing the listed ingredients in the listed proportions.

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<u>Ingredients</u>	<u>1</u> (%w/w)	<u>2</u> (%w/w)	<u>3</u> (%w/w)
Sorbitan mono-stearate (SMS)	0.5	0.5	0.5
Citric acid	11	11	11
NOBS	6	6	6
Polyacrylate (Acusol 445ND®)	11	11	11
Sodium percarbonate	31	31	31
C14-C16 Alcohol ethoxylated EO 25	2	-	-
C12-C16 Alcohol ethoxylated EO 11	-	2	-
C12-C16 Alcohol ethoxylated EO 50	-	-	2
Anionic (LAS/AS/AES)	8	8	8
DTPA	0.2	0.2	0.2
TAED	5	5	5
Minors and inerts	up to 100	up to 100	up to 100

<u>Ingredients</u>	<u>4</u> (%w/w)	<u>5</u> (%w/w)	<u>6</u> (%w/w)
Sorbitan mono-stearate (SMS)	2.5	-	-
Sorbitan monostearate EO 20 (SMS EO 20)	-	3.0	-
Sorbitan tristearate EO 20 (STS EO 20)	0.5	-	3.0
Citric acid	10	10	10
Polyacrylate (Acusol 445 ND®)	11	11	11
Silicate (amorphous; 1.6r)	0.4	0.4	0.4
Sodium percarbonate	31	31	31
NOBS	6	6	6
TAED	5	5	5
Anionic (LAS/AS/AES)	7	7	7
C14-C16(EO 25) Alcohol	2	2	2
Others, inerts and minors	up to 100	up to 100	up to 100

<u>Ingredients</u>	<u>7</u> (%w/w)	<u>8</u> (%w/w)	<u>9</u> (%w/w)
Sorbitan mono-stearate (SMS)	-	-	0.5
Citric acid	10	10	10
Polyacrylate (Acusol 445 ND)	11	11	11
Silicate (amorphous; 1.6r)	0.4	0.4	0.4
C12-C16 (EO 11) alcohol	-	2	2
C14-C16 (EO 25) alcohol	2	-	2
NaPS	2	2	-
Sodium percarbonate	31	31	31
Sodium sulphate	24	24	24
NOBS	6	6	6
TAED	5	11	5
Anionic (LAS/AS/AES)	8	8	8
Others, inerts and minors	up to 100	up to 100	up to 100

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TAED is tetracetyl ethylene

NOBS is n-nonanoyloxybenzenesulphonate

NaPS is sodium paraffin sulphonate

DTPA is Diethylene-triamine-Penta Acetic acid.

10

Soaking liquors are formed by diluting each time 45 g of the above compositions in between 3.5 lit. to 5.0 lit. of water. 0.5 to 2 Kg of fabrics are then each time immersed in said soaking liquor. The soaking periods for the soaking liquors comprising any of the above soaking compositions 1 to 6 or 9 are typically from

15

10 minutes to 24 hours.

For the soaking liquor comprising the soaking compositions 7 or 8 described herein before, the soaking time according to the process of soaking of the present invention is of more than 1 hour and preferably 4 to 24 hours.

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Finally, the fabrics are removed from the soaking liquors, rinsed with water and washed with a regular washing process, handwash or washing machine wash,

with a regular detergent, with or without re-using the soaking liquor, then said fabrics are left to dry. Excellent stain removal performance is obtained with these compositions on various stains including mud/clay stains as well as enzymatic stains and/or bleachable stains and the like.



WHAT IS CLAIMED IS:

1. A granular soaking composition comprising:
  - from 0.001% to 15% by weight of the total composition of a sorbitan ester according to the formula  $C_6H_9O_2 (C_2H_4O)_x R_1R_2R_3$ , wherein x is an integer of from 0 to 40,  $R_1$ ,  $R_2$  are independently OH or  $(C_n H_{2n+1})COO$ , and  $R_3$  is  $(C_n H_{2n+1})COO$  group, where n is an integer of from 11 to 17,
  - from 0.001% to 20% by weight of the total composition of an alkoxyated nonionic surfactant according to the formula  $RO-(A)_nH$ , wherein R is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 40 carbon atoms, A is an alkoxy group having from 2 to 10 carbon atoms, and wherein n is an integer from 9 to 100,
  - and an oxygen bleach.
2. A composition according to claim 1 which comprises from 0.01% to 10% by weight of the total composition of said sorbitan ester or a mixture thereof, preferably from 0.1% to 5% and more preferably from 0.5% to 4%.
3. A composition according to any of the preceding claims wherein said sorbitan ester is polyethoxylated (20) sorbitan tristearate, or polyethoxylated (20) sorbitan monostearate, or sorbitan monostearate, or sorbitan monopalmitate, or mixtures thereof.
4. A composition according to any of the preceding claims which comprises a non-ethoxylated sorbitan ester and an ethoxylated sorbitan ester.
5. A composition according to any of the preceding claims which comprises from 0.01% to 15% of said alkoxyated nonionic surfactant or a mixture thereof, preferably from 0.1% to 10%, and more preferably from 0.5% to 5%.

6. A composition according to any of the preceding claims wherein in said alkoxyated nonionic surfactant according to the formula  $RO-(A)_nH$ , R is a substituted or unsubstituted, saturated or unsaturated, linear or branched alkyl group or aryl group having from 6 to 40 carbon atoms, preferably from 8 to 25, more preferably from 10 to 20, n is an integer from 9 to 100, more preferably from 10 to 80 and most preferably from 10 to 30, and A is an alkoxy group having from 2 to 8 carbon atoms and preferably is propoxy and/or ethoxy.
7. A composition according to any of the preceding claims which comprises from 0.01% to 80% by weight of the total composition of an oxygen bleach or mixtures thereof, preferably from 5% to 45% and more preferably from 10% to 40%.
8. A composition according to any of the preceding claims wherein said oxygen bleach is an alkali metal salt of percarbonate.
9. A composition according to any of the preceding claims which further comprises an activator for said bleach up to a level of 30% by weight of the total composition.
10. A composition according to any of the preceding claims which further comprises at least one optional ingredient selected from the group consisting of acidifying agents, alkali metal salt of silicate, builders, soils suspending agents, fillers, other surfactants, optical brighteners, enzymes, chelating agents, dispersants, soil release agents, dyes, dye transfer inhibitors, pigments, perfumes and mixtures thereof.
11. A process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition according to any of the preceding claims, for an effective period of time, then removed from said soaking liquor.

12. A process according to claim 11 wherein said time ranges from 10 minutes to 24 hours, preferably 30 minutes to 24 hours, more preferably more than 1 hour up to 24 hours and most preferably 4 hours to 24 hours.
13. A process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition comprising an oxygen bleach and an alkoxyated nonionic surfactant according to the formula  $RO-(A)_nH$ , wherein R is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 40 carbon atoms, A is an alkoxy group having from 2 to 10 carbon atoms, and wherein n is an integer from 9 to 100, for more than 1 hour, preferably 2 hours to 24 hours and more preferably 4 hours to 24 hours, then removed from said soaking liquor.

## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/US98/02720

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 1/66, 1/74, 7/18, 7/54

US CL : 510/367, 375, 422

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/367, 375, 422

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,089,162 A (RAPISARDA et al) 18 February 1992, col. 4, lines 16-21, col. 6, lines 62-68, col. 7, lines 39-51, col. 7, line 66 - col. 8, line 2.	1-3 and 13
Y	EP 0 736 594 A1 (BISCARINI et al) 09 OCTOBER 1996, p.2, line 52 et seq, p.5, line 14 et seq, p.6, line 10	1-3
Y	JP 03287700 A (MINAGAWA et al) 18 DECEMBER 1991, English abstract-all	1-3
Y	JP 62001792 A (NISHIGUCHI et al) 07 January 1987, English abstract-all	1-3
Y,P	JP 10017894 A (OGURA et al) 20 January 1998, English abstract-all	1-3

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

24 APRIL 1998

Date of mailing of the international search report

22 MAY 1998

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/02720

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-12  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet)(1)XJuly 1992)★

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US91/02720

### B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

#### APS, CAS ONLINE

search terms: oxygen bleach, hydrogen peroxide, peroxyacid, perborate, percarbonate, sorbitan ester, sorbitan, polysorbate, sorbitan monopalmitate, polyethoxylated sorbitan tristearate, ethoxylated nonionic, alkoxylated nonionic, soaking/soaker composition